

# Ultra-precision $^{14}\text{CO}_2$ measurements in Clean-Air Samples: A Record of the Carbon Cycle and Anthropogenic Influences

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*A critical scientific question is what are the present day sources and sinks of carbon dioxide ( $\text{CO}_2$ ) in the natural environment and how will these sinks evolve under rising  $\text{CO}_2$  concentrations and expected climate change and ecosystem response. Sources and sinks of carbon dioxide impart their signature on the distribution, concentration, and isotopic composition of  $\text{CO}_2$ . Spatial and temporal trends (variability) provide information on the net surface (atmosphere to ocean, atmosphere to terrestrial biosphere) fluxes. The need to establish more reliable estimates of sources and sinks of  $\text{CO}_2$  has lead to an expansion of  $\text{CO}_2$  measurement programs over the past decade and the development of new methodologies for tracing carbon flows. These methodologies include high-precision  $p\text{CO}_2$ ,  $\delta^{13}\text{CO}_2$ , and  $[\text{O}_2/\text{N}_2]$  measurements on atmospheric constituents which when combined have allowed estimates of the net terrestrial and oceanic fluxes at decadal timescales. Major gaps in our understanding remain however, and resulting flux estimates have large errors and are comparatively unconstrained.*

*One potentially powerful approach to tracking carbon flows is based on observations of the  $^{14}\text{C}/^{12}\text{C}$  ratio of atmospheric  $\text{CO}_2$ . This ratio can be used to explicitly distinguish fossil-fuel  $\text{CO}_2$  from other sources of  $\text{CO}_2$  and also provide constraints on the mass and turnover times of carbon in land ecosystems and on exchange rates of  $\text{CO}_2$  between air and sea. Here we present  $^{14}\text{C}/^{12}\text{C}$  ratios at 1-2‰ on archived and currently collected air samples from the Scripps Institution of Oceanography  $\text{CO}_2$  Flask Network, and ‘entrepreneurial’ samples collected from the stratosphere and the free troposphere.*

## General Background

Carbon dioxide ( $\text{CO}_2$ ) is the most important man-made greenhouse gas influencing global climate. The atmospheric concentration of  $\text{CO}_2$  has risen from ~280ppm in the early 1800s to ~385ppm today primarily from the utilization of fossil fuels, cement production, and land use practices. Paleo-atmospheric measurements on air bubbles trapped in ice cores document that present values are the highest that they have been in at least the last 740000 years and the rate of change is unprecedented, even on glacial-interglacial time scales. Carbon dioxide concentrations are currently rising at ~1.5 ppm/yr, a rate which is controlled not just by the emissions from biomass and fossil-fuel burning, but also by the variable exchanges of  $\text{CO}_2$  with the oceans and land biota. Less than half of the estimated ~280 petagrams (Gt) of fossil-fuel carbon and ~190 Gt of land-use carbon reside in the atmosphere; the remaining anthropogenic carbon has been

partitioned into the terrestrial biosphere and oceans. Uptake by the terrestrial biosphere is a consequence of excess primary production relative to respiration and decomposition and is partitioned into fast (decades) and slow (millennia) carbon pools. Ocean uptake is accomplished by physical (air-sea) processes and is governed by carbonate chemistry, ocean dynamics, and biological productivity. Carbon sequestration in the ocean has a residence time in keeping with the residence time of the respective water masses. The deep interior ocean residence time is centuries to millennia and that of the shallow circulation on the order of decades. Upwelling significantly influences the interannual ocean CO<sub>2</sub> flux. Time series of precisely measured atmospheric constituents are critical to understand the fate and transport of (anthropogenic) carbon in the contemporary carbon cycle. With the pioneering work of C. Keeling atmospheric CO<sub>2</sub> concentrations have been continuously measured at Mauna Loa and the South Pole since 1957. These initial stations have grown into a loosely confederated network of surface stations with quasi-global coverage. The stable carbon isotope (<sup>13</sup>C:<sup>12</sup>C) ratio (δ<sup>13</sup>C) of atmospheric CO<sub>2</sub> on flask samples was added in the late 1970s. The δ<sup>13</sup>C of atmospheric CO<sub>2</sub> can be used to estimate the partitioning of carbon uptake between the terrestrial biosphere and ocean. The rationale relies on fractionation during photosynthesis, where the δ<sup>13</sup>C of plants that follow the C3 photosynthetic pathway are 1.8‰ more negative relative to atmospheric CO<sub>2</sub>. Air-sea exchange of CO<sub>2</sub> involves only a minor fraction effect. The combustion of fossil fuel results in an overall decrease in δ<sup>13</sup>C since fossil fuel carbon δ<sup>13</sup>C is more negative than atmospheric CO<sub>2</sub>. [CO<sub>2</sub>] and δ<sup>13</sup>CO<sub>2</sub> measurements with a prescribed turnover in the terrestrial biosphere and ocean can result in one unconstrained solution of the partitioning of the net carbon fluxes.

Measurements of the concentration of atmospheric oxygen [O<sub>2</sub>], which began in the early 1990s, can provide complementary information to [CO<sub>2</sub>] and δ<sup>13</sup>CO<sub>2</sub>. The concentration of oxygen in the atmosphere reflects the net biosphere production (photosynthesis – respiration) balanced by that consumed by fossil fuel combustion. CO<sub>2</sub> uptake by the ocean has no direct effect on atmospheric [O<sub>2</sub>] whereas terrestrial uptake yields a net flux to the atmosphere. It is assumed that the oceanic biosphere remains nutrient limited with no net effect on atmospheric [O<sub>2</sub>] trends.

Seasonal to interannual variability of the respective net fluxes is much larger than the uncertainty in the decadal averages which has made it difficult to quantify sinks and sources on shorter annual timescales. Complications to δ<sup>13</sup>C, [O<sub>2</sub>], and [CO<sub>2</sub>] based carbon flux estimates exist. First, in addition to C3 plants there are C4 and CAM plants that discriminate much less against <sup>13</sup>C than C3 plants (*ie.*, δ<sup>13</sup>C is more positive), thus for meaningful analysis the relative distribution of C3 and C4 plants must be known. Second, although the oceanic disequilibrium value is close to zero it changes with changing atmospheric δ<sup>13</sup>CO<sub>2</sub>. Common to both [O<sub>2</sub>] and δ<sup>13</sup>C methods is a requirement that the oceanic and terrestrial carbon residence times be provided. Finally, there is an implicit assumption that the fossil fuel fluxes are well known. Briefly touched upon earlier was the fact that the net fluxes to/from the ocean / terrestrial biosphere are two uni-directional fluxes (*e.g.* F<sub>netatmbio</sub> = F<sub>atmbio</sub> + F<sub>bioatm</sub>). If we were to construct a system of linear equations we would find that an accurate and precise solution is underconstrained. An additional carbon tracer would allow for more accurate estimates of the net fluxes.

Radiocarbon ( $t_{1/2}$  5730yrs), is produced naturally in the stratosphere by the collision between cosmic-ray generated secondary neutrons and  $^{14}\text{N}$ . Upon formation  $^{14}\text{C}$  is rapidly oxidized to  $\text{CO}_2$  and exchanges with the terrestrial biosphere and oceans. Atmospheric testing doubled the  $^{14}\text{C}$  content in the atmosphere from its  $^{14}\text{C}/^{12}\text{C}$  ratio of  $1.18 \times 10^{-12}$ . Following the atmospheric weapons test ban in 1963, the  $^{14}\text{C}/^{12}\text{C}$  ratio, (normally reported as  $\Delta^{14}\text{C}$  which includes a correction for mass dependent fractionation), has decreased. Atmospheric  $\Delta^{14}\text{C}$  reflects variations in fossil fuel emissions ( $^{14}\text{C}$ -free), ocean-atmosphere exchange, stratosphere-troposphere mixing, and terrestrial ecosystem fluxes. As a consequence of the redistribution of “anthropogenic”- $^{14}\text{C}$  into and with the terrestrial and ocean reservoirs, the spatio-temporal variability of  $^{14}\text{CO}_2$  has decreased. In the mid 1960s across the mid to high latitudes of the northern hemisphere the seasonal cycle of  $\Delta^{14}\text{C}$  was in excess of 50‰ with similar phasing of the seasonal cycle; maximum values were reached in the boreal summer and a minimum in winter. This seasonality was driven by a combination of seasonal (spring-summer) troposphere-stratosphere exchange and the increased use of fossil fuel during winter. In more recent decades, the seasonal amplitude has decreased albeit regions that experience larger fossil fuel consumption tend to have a larger peak to trough amplitude than “clean-air” locations.

#### *Radiocarbon as a Carbon Cycle Tracer*

**(i) Constrain fossil-fuel emissions.**  $\Delta^{14}\text{C}$  is probably the best available tracer for resolving fossil-fuel  $\text{CO}_2$  from other sources of  $\text{CO}_2$ . While other tracers, like  $\text{O}_2/\text{N}_2$  and  $^{13}\text{C}/^{12}\text{C}$ , are useful for distinguishing land versus oceanic components of the  $\text{CO}_2$  variations, these tracers do not, in fact, distinguish between land biospheric and fossil-fuel components. Neither do current inverse model calculations. To separate land exchanges into fossil-fuel and land biospheric components, using inverse techniques or using  $\text{O}_2/\text{N}_2$  or  $^{13}\text{C}/^{12}\text{C}$  data, it is necessary to apply corrections for the effects from fossil-fuel. Typically these corrections are based on statistical compilations for the distribution of fossil-fuel burning in combination with atmospheric transport models. Both of these have sizeable uncertainties, especially at smaller space (regional) and time (seasonal) scales. Model simulations indicate that fossil-fuel burning should produce  $\Delta^{14}\text{C}$  deficits of 15 to 25‰ over N. America and Eurasia. By helping to resolve the fossil-fuel contribution to  $\text{CO}_2$  variability  $\Delta^{14}\text{C}$  measurements could play a direct role in improving estimates from inversion calculations of the land biospheric flux over North America. Measurements would also provide independent constraints on rates of fossil-fuel burning.

**(ii) Constrain rates of ocean ventilation and mixing.** While atmospheric  $\Delta^{14}\text{C}$  is not sensitive to the net uptake of anthropogenic  $\text{CO}_2$  by the oceans, it is sensitive to the gross (*i.e.* two-way) exchanges that swap  $^{14}\text{C}$  atoms with  $^{12}\text{C}$  atoms across the air-sea interface. These exchanges tend to lower atmospheric  $\Delta^{14}\text{C}$  since the ocean is a large reservoir of  $^{14}\text{C}$  deficient carbon. The effectiveness of this exchange depends both on rates at which  $\text{CO}_2$  molecules are exchanged across the air-sea interface as well as on rates of internal ocean mixing. These gross air-sea exchanges are a major driver of the long-term decrease in atmospheric  $\Delta^{14}\text{C}$  in recent decades. The exchanges also can contribute to the

$\Delta^{14}\text{C}$  gradients within the atmosphere. Measurements at background stations by the Heidelberg group show that the lowest  $\Delta^{14}\text{C}$  values are found, not over the Northern Continents, as expected from fossil-fuel burning, but rather over the Southern Ocean, where the high rates of vertical mixing and air-sea exchange cause a regional reduction in  $\Delta^{14}\text{C}$  in the overlying air. The magnitude of this regional deficit is sensitive to rates of gas exchange and ocean mixing. The measurements can thus contribute to helping to characterize these processes and their stability over time. These same processes also control the rate at which anthropogenic  $\text{CO}_2$  is taken up by the ocean, so atmospheric  $\Delta^{14}\text{C}$  measurements, especially when combined with measurements of  $\Delta^{14}\text{C}$  in the water, can contribute to improved estimates of oceanic anthropogenic  $\text{CO}_2$  uptake.

**(iii) Constrain turnover-times and size of land biosphere.** Atmospheric  $\Delta^{14}\text{C}$  is sensitive to gross exchange of  $\text{CO}_2$  with the land biosphere. The imprint on atmospheric  $\Delta^{14}\text{C}$  of these exchanges is a function of the turnover times and size of the various land carbon pools in land plants and soils and a function of recent atmospheric  $\Delta^{14}\text{C}$  history. In the first few decades after the bomb tests, the land biosphere served to reduce atmospheric  $\Delta^{14}\text{C}$  by absorbing a fraction of the bomb  $^{14}\text{C}$  excess. More recently, the land biosphere has switched to being a source. Excess  $^{14}\text{C}$  taken up by land biota in the first few decades after the bomb tests is now being given back to the atmosphere. The return of decade-old carbon from the land biota is greatest in the summer, when respiration rates are highest, so this exchange contributes to the seasonality of atmospheric  $\Delta^{14}\text{C}$ . Measurements of the seasonality in  $\Delta^{14}\text{C}$ , its spatial distribution, and its evolution over time can be used to improve our understanding of turnover times and sizes of land biosphere carbon pools, which in turn can improve our predictions of the role of land biota as a potential sink for anthropogenic  $\text{CO}_2$ .

### Technical Objectives

The primary analytical objective was to analyze archived ~biweekly  $\text{CO}_2$  samples from the SIO  $\text{CO}_2$  network (Figure 1) which will provide a baseline of the latitudinal and temporal variability in  $\Delta^{14}\text{C}$  for “clean air” sites. These data reflect what is in effect is a carbon isotope accounting of the net fluxes of carbon between reservoirs (ocean, terrestrial) and ‘dilution’ of  $^{14}\text{C}$  with fossil fuel derived carbon dioxide and ‘enrichment’ from the stratosphere (where  $^{14}\text{C}$  is naturally formed).

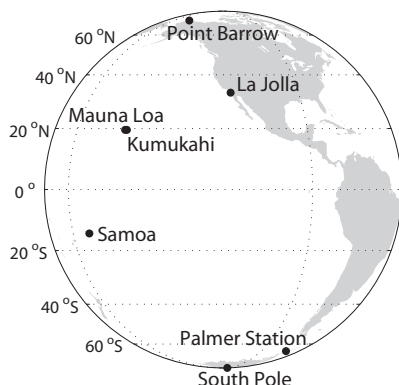


Figure 1. Location of the Scripps  $\text{CO}_2$  sites where we have developed  $\Delta^{14}\text{C}$  time-series.

The long-term trend in all of the time-series approaches  $-5.5\text{‰}$  per year with Point Barrow exhibiting the most consistent and largest seasonal cycle (Figure 2). The larger seasonal cycle (relative to *eg.*, Mauna Loa, American Samoa) is to some extent a reflection of the asymmetry of fossil fuel utilization with most of the utilization in the northern hemisphere. Atmospheric circulation brings high  $\text{CO}_2$  air from Eurasia to the Arctic.

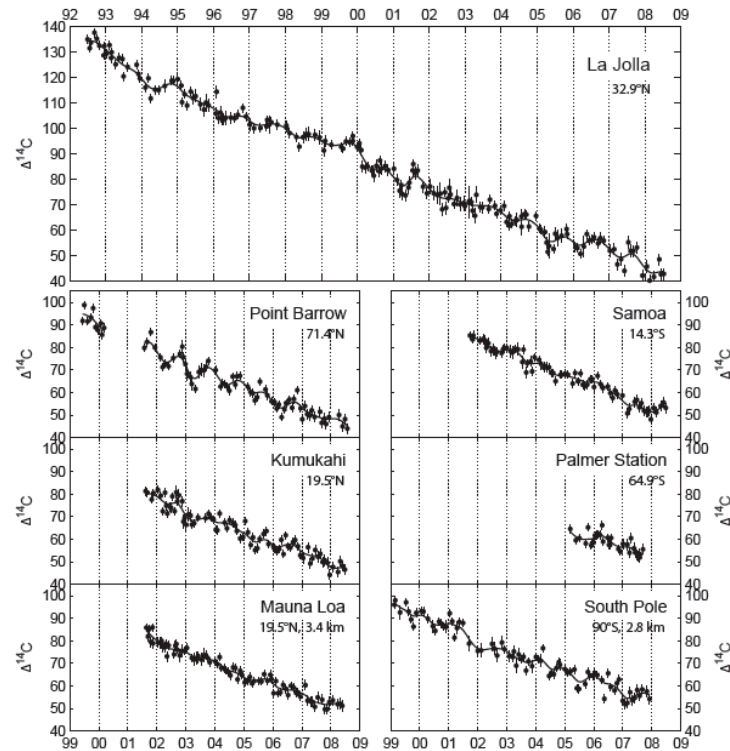


Figure 2. Composite  $\Delta^{14}\text{C}$  time-series of the SIO  $\text{CO}_2$  stations (*Graven et al., in preparation*).

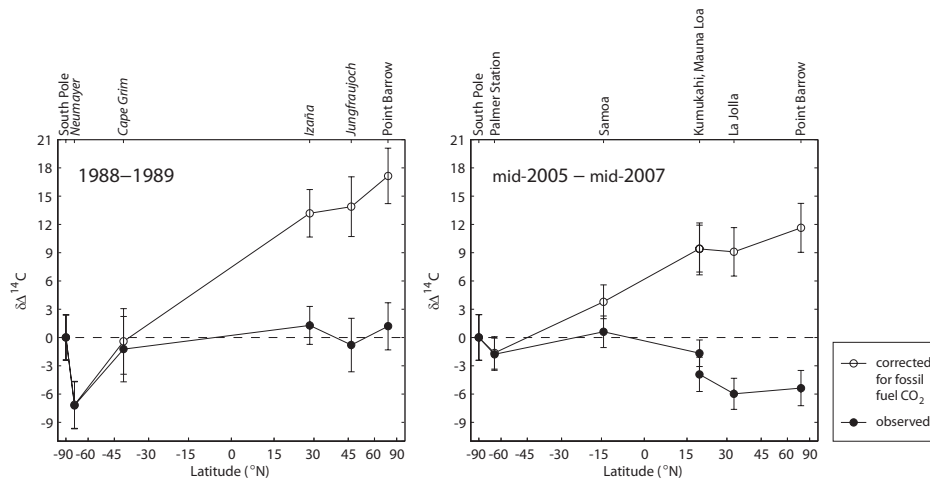


Figure 3. Example of the evolution of the latitudinal gradient between 1988-1989 and 2005-2007 relative to the South Pole (*Graven et al., in preparation*). The effect of fossil fuel  $\text{CO}_2$  is estimated from the TransCom emission basis functions.

The latitudinal gradient (Figure 3) includes a difference in the influence of ocean to atmosphere  $^{14}\text{CO}_2$  exchange in the southern ocean and the influence of more fossil fuel  $\text{CO}_2$  emissions in 2005-2007 versus 1988-1989. Mean  $\Delta^{14}\text{C}$  in 1988-89 and mid-2005 to mid-2007 was calculated by the mean of a linear trend and annual harmonic fit to the observations at SIO stations and at 4 stations in the Heidelberg network (Meijer et al., *Radiocarbon* 2004; Levin and Kromer, *Radiocarbon*, 2004; Levin et al., *Radiocarbon after four decades*, 1992). Corrections for local fossil fuel  $\text{CO}_2$  were determined using the results of the TRANSCOM 3 experiments (Gurney et al., *Tellus*, 2003). The results document a shift in the  $\Delta^{14}\text{C}$  gradient. Clearly seen in the data is a decrease in the minimum off the coast of Antarctica. This could be interpreted as a decrease in the rate of upwelling and exchange of (lower- $^{14}\text{C}$ )  $\text{CO}_2$  with the atmosphere. With regards to future measurement programs: combining atmospheric and oceanic measurements in the Southern Hemisphere will provide a means to ‘monitor’ and test the hypothesis that as climate warms due to anthropogenic activities that the southern ocean will become more stable (due to both warming and freshening which have an additive effect to decrease density) and thus decrease the overturning and deep-water production in the Southern Ocean.

We have begun exploring the long-term  $\Delta^{14}\text{C}$  trends using simple box models (Figure 4). We have calculated contributions to the global trend in  $\Delta^{14}\text{C}$  using reported fossil fuel emissions (Marland et al., CDIAC, 2008), the relationship between observed neutron flux and cosmogenic  $^{14}\text{C}$  production (Lowe et al., *Radiocarbon*, 2002), a 2-box model of the stratosphere (Randerson et al., *GBC*, 2002), a 1-box model of the biosphere (16-35 yr residence time) and a 43-box diffusion model of the ocean with eddy diffusion coefficients of 3000-4000  $\text{m}^2 \text{yr}^{-1}$  (Oeschger et al., *Tellus*, 1975) and  $\text{CO}_2$  piston velocities of 15.1-18.1  $\text{cm hr}^{-1}$  (Naegler, *Tellus*, 2009). The influence of ocean  $^{14}\text{CO}_2$  exchange has weakened over time due to the uptake and redistribution of ‘bomb- $^{14}\text{C}$ ’ in the ocean. Surface ocean values in much of the mid and low-latitude oceans are now very similar to the atmosphere, and thus the isoflux is near neutral. Regions that are still significantly lower than atmospheric  $\Delta^{14}\text{C}$  include the sub polar regions of the north Pacific and the Southern Ocean. Fossil fuel emissions were the strongest influence on the  $\Delta^{14}\text{C}$  trend. Oceanic exchange also reduced  $\Delta^{14}\text{C}$ , but the effect weakened considerably between 1992-2007. Relatively steady, positive influences of biospheric and stratospheric exchange and tropospheric production mediated the influences of the ocean and fossil fuels. Within the assumptions of the simple box models, the summed trend weakened between 1992-96, then stayed largely constant. It corresponded to the observed trend at La Jolla except during periods of rapidly declining  $\Delta^{14}\text{C}$ . The fitted trends at La Jolla are at the lower end of the modeled range, suggesting negative influences may be underestimated, or positive overestimated. Uncertainties relate to carbon turnover rates, NPP, strat-trop gradients, fossil fuel emissions and air-sea fluxes and could be improved using constraints from further observations and analyses of  $\Delta^{14}\text{CO}_2$ .

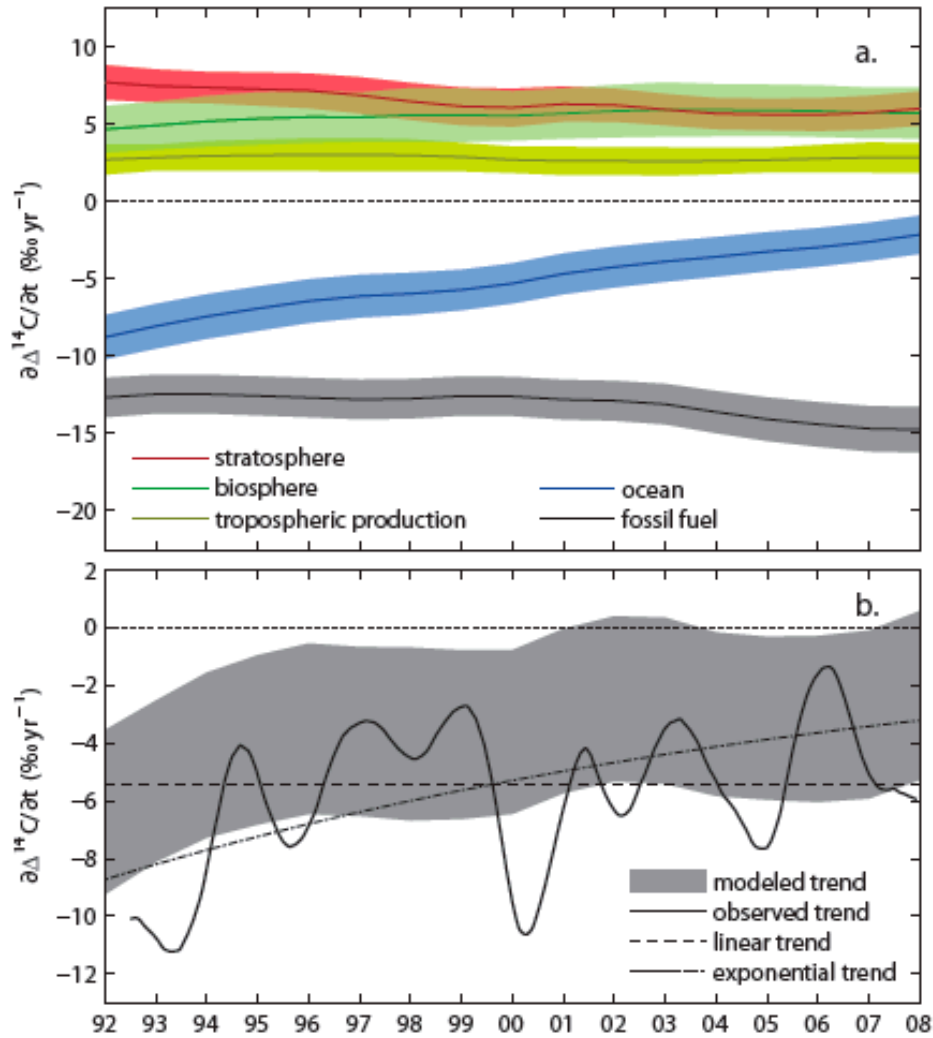


Figure 4. Modeled components of the global trend in  $\Delta^{14}\text{C}$  (a); filled areas showed uncertainties or plausible values. Sum of components of the modeled trend (b). Also plotted are the seasonally adjusted spline trend and the linear and exponential trends fit to the observations at La Jolla (slope of  $5.5 \text{ ‰ yr}^{-1}$  and e-folding time of 16.4 yr). Graven et al., in preparation for *J. Geophys. Res.*

As an illustrative example of attributing the source of  $\text{CO}_2$  in a parcel of air, we participated in vertical (aircraft) profile and sampling in an urban (Denver, CO) and rural (Kemmerling, CO) setting. A simple endmember mixing model was then constructed to partition  $\text{CO}_2$  deviations relative to the free-troposphere (Figure 5). The inclusion of  $^{14}\text{CO}_2$  measurements allows the explicit estimation of fossil fuel  $\text{CO}_2$  addition relative to eg., night time respiration or photosynthesis ( $\text{CO}_2$  uptake by plants).

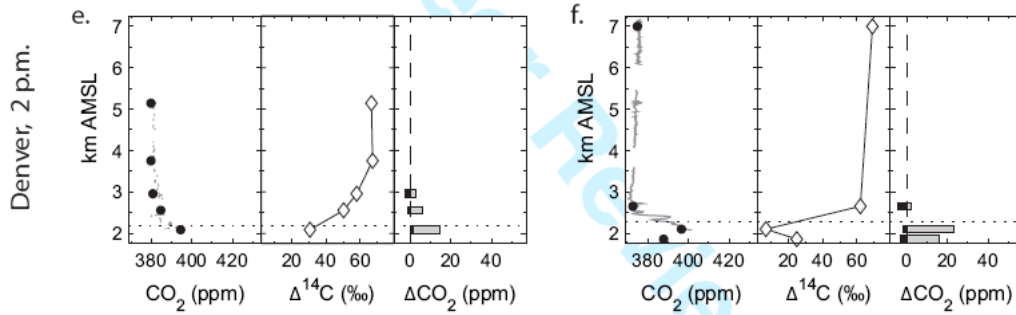


Figure 5. Early afternoon vertical profiles of  $\text{CO}_2$  (thin grey in situ aircraft analyses, solid symbols flasks),  $\Delta^{14}\text{CO}_2$ , and fossil fuel  $\text{CO}_2$  (gray bar) and biosphere (black bar) partitioning estimated from free troposphere (background) and diurnal respiration endmembers using  $\Delta^{14}\text{C}$  for May 20 (e) and July 20 (f) 2004 over Denver Colorado. Dashed line is the approximate position of the boundary layer. From Graven *et al.*, *Tellus* (2009).

We are analyzing and modeling nearly sixty (60)  $\Delta^{14}\text{CO}_2$  measurements from cryogenic whole air sample (CWAS) balloon samples from flights in Fall of 2003, 2004, and 2005 out of Fort Sumner, New Mexico ( $34^\circ\text{N}$ ) (Figure 6). These are one of the first sets of  $^{14}\text{CO}_2$  measurements in the stratosphere in the "post post-bomb era" – that is, for our purposes here, since the stratosphere has purged itself of at least the "first generation" of  $^{14}\text{C}$  generated by atmospheric weapons testing in the 1950s and early 1960s, and the first  $^{14}\text{CO}_2$  dataset for which simultaneous measurements of other long-lived species are also available that aid in (1) interpreting the atmospheric variations captured, (2) comparing the observations with global-scale atmospheric models using modern ideas about tracer-tracer correlations, and (3) quantifying the  $^{14}\text{CO}_2$  flux to the troposphere. Indeed, the last measurements of stratospheric  $^{14}\text{CO}_2$  available before now are from early 1974 [e.g., Johnston, 1989], a time when stratospheric  $^{14}\text{CO}_2$  was still perturbed by atmospheric weapons testing.

For example, for 2004 and 2005 we have used the observed correlation between the  $\Delta^{14}\text{C}$  and  $\text{N}_2\text{O}$  measurements in Figure 3 to estimate the annual mean net flux of  $^{14}\text{CO}_2$  between the stratosphere. Plumb and Ko (*J. Geophys. Res.*, 1992) have shown that the slope of the compact relationship between two long-lived tracers in slope-equilibrium is equal to the ratio of net vertical fluxes of the two species. The net vertical  $\text{N}_2\text{O}$  flux is known independently to be  $13.1 (\pm 25\%) \text{ TgNyr}^{-1}$  (Prather and Ehhalt, *IPCC.*, 2001), so that the net vertical flux for the other species of interest can be estimated from the value of the slope of its correlation with  $\text{N}_2\text{O}$ . This approach has been used in several applications in estimating fluxes of  $\text{O}_3$  (Olsen *et al.*, *J. Geophys. Res.*, 2001), meteoritic material (Murphy and Fahey, *J. Geophys. Res.*, 1994), and  $\text{N}_2\text{O}$  isotopologues (Park *et al.*, *J. Geophys. Res.*, 2004) from the stratosphere to the troposphere. Since air is returning to the troposphere from the lower stratosphere, observations for  $\text{N}_2\text{O}$  mixing ratios  $> 250 \text{ ppbv}$  are generally used. From our new dataset (shown in Figure 7) we derived a net  $^{14}\text{CO}_2$  flux between the stratosphere and troposphere of  $1.6 \times 10^{17} \text{ } \mu\text{mole CO}_2 \text{ yr}^{-1} (\pm 25\%)$ . This yields a stratospheric production rate of  $188 \text{ mol } ^{14}\text{CO}_2 \text{ yr}^{-1} (\pm 25\%)$  or  $1.1 \pm 0.3 \times 10^{26} \text{ atoms } ^{14}\text{C yr}^{-1}$  and a global production rate of  $2.2 \pm 0.6 \times 10^{26} \text{ atoms } ^{14}\text{C yr}^{-1}$  (assuming the ratio of stratospheric to upper tropospheric production is 0.5



to 0.6 (eg., Masarik and Beer, *J. Geophys. Res.* 1999).

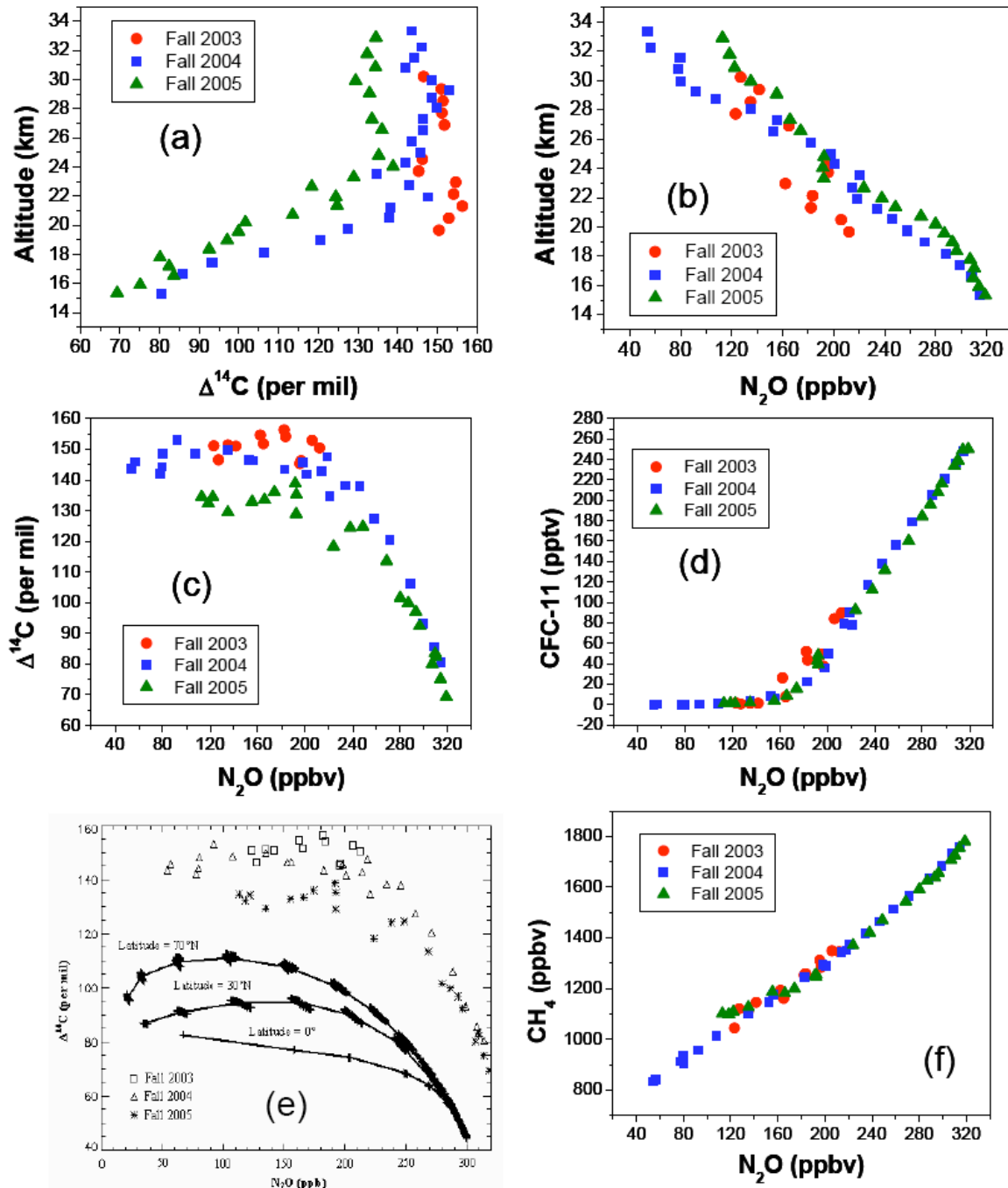


Figure 6. (a)  $\Delta^{14}\text{C}$  of  $\text{CO}_2$  and (b)  $\text{N}_2\text{O}$  vs altitude for samples collected from the CWAS at 34°N (Fort Sumner, New Mexico). Also shown are (c)  $\Delta^{14}\text{C}$  of  $\text{CO}_2$ , (d) CFC-11, and (f)  $\text{CH}_4$  vs.  $\text{N}_2\text{O}$ . (e) Preliminary results from LLNL's IMPACT 3D model with a(n unrealistic) globally-averaged, latitude-independent  $^{14}\text{C}$  source, showing  $\Delta^{14}\text{C}$  binned and averaged as a function of  $\text{N}_2\text{O}$  at 0°, 30°N, and 70°N (+ with lines); symbols are observations. Even with the unrealistic  $^{14}\text{C}$  source distribution, the model results show that mixing of older, higher latitude air into the midlatitudes will result in an increase in  $\Delta^{14}\text{C}$  in such filaments encountered by the CWAS instrument over Ft. Sumner (rather than the more familiar behavior of

"tracertracer" mixing lines of gases with tropospheric sources and stratospheric sinks.

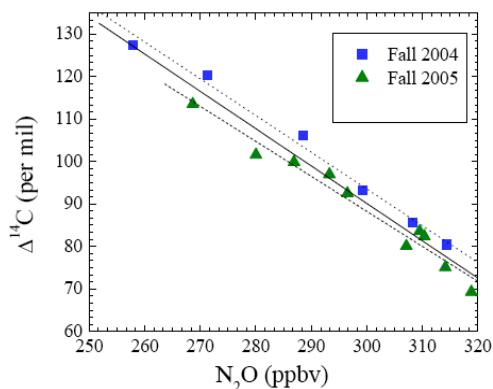


Figure 7:  $\Delta^{14}\text{C}$  vs  $\text{N}_2\text{O}$  for  $\text{N}_2\text{O} > 250$  ppbv for data in Figure 6; also shown are the linear least-squares fits for the 2004 data (dotted line; slope =  $-0.87 \pm 0.05$ ), the 2005 data (dashed line; slope =  $-0.82 \pm 0.05$ ), and for the combined data set (solid line; slope =  $-0.88 \pm 0.05$ ).

### Summary:

$\Delta^{14}\text{CO}_2$  analyses are a powerful and significantly under utilized tool for carbon cycle studies and ‘attribution,’ or partitioning, of  $\text{CO}_2$  in atmospheric  $\text{CO}_2$  between fossil fuel, ‘background’, and biospheric processes. There is mounting interest of attributing local to regional fossil fuel  $\text{CO}_2$  emissions using  $^{14}\text{C}$  and other tracers in a “top-down” framework to i) provide a check on bottom up inventories, and ii) to provide a better ‘local’ estimate of  $\text{CO}_2\text{ff}$  to more accurately constrain the terrestrial biosphere flux. As a model diagnostic,  $^{14}\text{CO}_2$  and similar tracers are unparalleled in exploring (via empirical relationships) atmospheric transport model deficiencies (eg., venting of the planetary boundary layer, convection, and basic transport issues). Overtures have been made to NOAA/ESRL scientists and to both NOAA and DOE program managers for an integrated National Atmospheric Network that routinely includes  $^{14}\text{C}$ . Such an activity would be done in support of the overall objectives of the North American Carbon Program and coordinated with other USGCRP activities.

### Education and Outreach:

The analyses made under this research were primary data (activities) for the following theses:

*Advancing the use of radiocarbon in studies of global and regional carbon cycling with high precision measurements of  $^{14}\text{C}$  in  $\text{CO}_2$  from the Scripps  $\text{CO}_2$  Program.* Heather D. Graven, PhD, 2008, University of California – San Diego.

*Measurements and analysis of post-bomb era stratospheric  $^{14}\text{CO}_2$ : Applications to atmospheric chemistry and transport and carbon cycle dynamics* Lauren L. Comfort, MSc 2008, University of California- Berkeley.

### Cumulative Abstracts and Publications Supported by this Research:

*Additional manuscripts using the data collected under this project are in preparation but are not listed.*

H.D. Graven<sup>†</sup>, T. P. Guilderson, and R.F. Keeling, 2009. Trends and gradients in  $\Delta^{14}\text{C}$  of atmospheric  $\text{CO}_2$  observed by the Scripps global flask network. Poster presentation, 20<sup>th</sup> International Radiocarbon Conference, Kailua-Kona, Hawai'i.

H.D. Graven<sup>†</sup>, B.B. Stephens, T.P. Guilderson, T.L. Campos, D.S. Schimel, J.E. Campbell, and R.F. Keeling, 2009. Vertical profiles of biogenic and fossil fuel-derived  $\text{CO}_2$  from airborne measurements of  $\Delta^{14}\text{CO}_2$  and  $\text{CO}_2$  above Colorado. *Tellus B* Mar 5 2009 DOI: 10.1111/j.1600-0889.2009.00421.x.

H.D. Graven<sup>†</sup>, T.P. Guilderson, and R.F. Keeling, 2007. Methods for high precision measurements of atmospheric  $^{14}\text{CO}_2$  at LLNL. *Radiocarbon*, 49, 349-356.

H.D. Graven<sup>†</sup>, T.P. Guilderson, and R.F. Keeling, 2007. New Observations of Regional Variability in  $\Delta^{14}\text{C}$  of Background  $\text{CO}_2$  from the Scripps  $\text{CO}_2$  Program. *EOS Trans. AGU* 88(52), B51E-04.

D. Bergmann, P. Cameron-Smith, T.P. Guilderson, K. Grant, and H. Graven, 2007. Constraining regional fossil fuel  $\text{CO}_2$  emissions and choosing an optimal measurement network using  $^{14}\text{C}$  observations, modeling, and inversions. *EOS Trans. AGU* 88(52), B51E-03.

H.D. Graven<sup>†</sup>, R.F. Keeling, T.P. Guilderson, 2007.  $\Delta^{14}\text{CO}_2$  From the Scripps  $\text{CO}_2$  Program. International  $\text{CO}_2$  Experts Meeting, 14th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques, Helsinki.

T.P. Guilderson, H.D. Graven, and R. F. Keeling, 2007.  $^{14}\text{CO}_2$  Measurements in Clean Air Samples: A Record of the Carbon Cycle and Anthropogenic Influences. NOAA

Office of Global Program's North American Carbon Program Meeting, Silver Spring Maryland

H.D. Graven<sup>†</sup>, R.F. Keeling, and T.P. Guilderson. Developing high precision measurements of  $^{14}\text{CO}_2$  for carbon cycle studies. North American Carbon Program PI meeting, Colorado Springs CO, January 2007.

H. D. Graven<sup>†</sup>, B. Stephens, R. F. Keeling, T. P. Guilderson, T. L. Campos, and D. S. Schimel, 2006. Identifying  $\text{CO}_2$  Sources With Vertical Profiles of  $\Delta^{14}\text{CO}_2$  Above Colorado. *EOS Trans. AGU*, 87(52) B41G-08. *Note: session chair Scott Denning submitted this presentation as a candidate for best student oral presentation*

X. Xu, S.E. Trumbore, H.O. Ajie, and S.C. Tyler.  $\Delta^{14}\text{C}$  of Atmospheric  $\text{CO}_2$  over the subtropical and equatorial Pacific from fall 2002 to winter 2004. Oral presentation, 19<sup>th</sup> International Radiocarbon Conference, April 3-7, 2006. Oxford UK.

H.D. Graven<sup>†</sup>, T.P. Guilderson and R.F. Keeling, 2006. High-precision AMS- $^{14}\text{C}$  measurements on atmospheric  $\text{CO}_2$  samples at CAMS. Oral presentation, 19<sup>th</sup> International Radiocarbon Conference, April 3-7, 2006. Oxford UK.

T.P. Guilderson, H.D. Graven, K. Caldeira, R.F. Keeling, and C.D. Keeling.  $^{14}\text{CO}_2$  Measurements on the Scripps Flask Archive – A Unique Tool to Study the Carbon Cycle. Poster presented at the 17<sup>th</sup> *Annual Frontiers of Science Symposium of the National Academy of Sciences*, October 27-29, 2005. Irvine CA.

H.D. Graven<sup>†</sup>, T.P. Guilderson, R.F. Keeling, and C.D. Keeling. Precise Measurement of Background  $^{14}\text{CO}_2$ . Poster presented at the 7<sup>th</sup> International Conference on Carbon Dioxide, September 25-30, 2005. Boulder CO.

T.P. Guilderson, H.D. Graven, R.F. Keeling, and C.D. Keeling,  $^{14}\text{CO}_2$  Measurements on the Scripps Flask Archive – A status report. Poster presented at the 10<sup>th</sup> International Conference on Accelerator Mass Spectrometry, September 5-10, 2005. Berkeley CA.

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